

**9th International Symposium on New Materials and Nano-Materials for  
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**Feasibility Study to Use Hydrogen as Alternative Source of Energy in Mexico**

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ABSTRACT

Mexican hydrogen industry currently produces 500,000 tons of hydrogen per year. Hydrogen is primarily used as a feedstock, intermediate chemical, or specialty chemical in: chemical production, petroleum refining, metal treating, electronic applications, and food and soap/detergent industries. Main hydrogen production method is steam methane reforming (SMR). Other methods includes: gasification of fossil fuels, partial oxidation and water electrolysis. Some of the produced hydrogen could be used like alternative energy source. United States, Spain and Germany already use it like fuel, this hydrogen is mainly produced by SMR, however there are also projects focuses to produce hydrogen from electrolysis method coupling renewable energies sources (solar energy, wind power, wave energy, etc). In Mexico, SMR is also the main process to obtain hydrogen, 98%, nevertheless Mexichem Plant and Quimikao Plant (where hydrogen is a by-product of Sodium Hypochlorite Process and feedstock to fats hydrogenations respectively) are planning use the hydrogen as fuel, they have several projects where the hydrogen is a potential energetic to reduce energy spending of grid from CFE through fuel cells use, decreasing the energy from the second consumer of electricity in Jalisco. Exist production potential of hydrogen in the country; the SMH (Mexican Hydrogen Society) is working to incorporate into Mexican Legislation the hydrogen as alternative source of energy in Mexico.

*Keywords: Hydrogen legislation, electrolysis, renewable energies sources.*



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## **1. Introduction**

The hydrogen production capacity in mexican refineries in 2011 was 183 MMSCFD (million standard cubic feet per day), used for hydrodesulfurization process in refineries, this process and the largest hydrogen consumer not only in Mexico but the word. Same year, United States generated in refineries 4,114.3 MMSCFD, placing it in the first place worldwide alone followed by Japan and South Korea 1,472.8 MMSCFD and 995. 5 MMSCFD respectively, México is in the global site 16 in the production of hydrogen. In 2010 word production of hydrogen was 13 TSCFD (trillion standard cubic feet per year) [1].

The highest percentage of hydrogen is not used as energy, but as raw material in the hydrodesulfurization process oil and other industrial uses are among the production of hydrochloric acid, production of ammonia, hydrogen peroxide and as feedstock in the hydrogenation of fats and oils. Hydrogen production in refineries where has the highest consumption in the word is through the process of reforming of natural gas SMR, only in the United States 2010 were used 154.503 million cubic feet of natural gas to produce hydrogen, this process in 2009 were consumed 143.004 million cubic feet of gas natural one year before, in 2008 were consumed 188.075 million cubic feet of natural gas to produce hydrogen [2].

## **2. Analysis of hydrogen production technology**

The total cost of investment (TCI) of the following hydrogen production technologies specified in US \$/GJ. The TCI is a measure of capital cost of plant per unit of hydrogen produced, processed or stored [7].

### **2.1. Hydrogen from Steam Methane Reforming SMR**

The SMR process is cheaper process with respect to others such as gas gasification and pyrolysis also more environmentally friendly, natural gas, methane at a higher rate (94.9% methane, 2.5% ethane and other gases in concentrations less than 0.2% ) is effective to produce hydrogen as it is widely available easy to used and has an extensive hydrogen to carbon ratio which minimizes the formation of CO<sub>2</sub> as a by-product and thus emissions of greenhouse gases are minor compared to the pyrolysis process that needs to heavier hydrocarbons. Over 80% of the hydrogen production is achieved by the reforming process of natural gas. There are four basic steps: pretreatment, where the gas is treated catalytically with hydrogen to remove sulfur compounds, the desulfurized gas is reformed with steam mixing and then pass through a nickel-alumina catalyst to produce a hydrogen-rich gas and as a final step hydrogen purification. In the process using a furnace to raise the temperature of the gas in the first step-pretreatment,



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heat also functions to produce steam which is used in the reformation and gas conversion, the use of gas natural furnace fuel and the process gas which is a residue of the last process of purification of hydrogen [3-4].

The scheme presented in figure 1, shows the basic steps of the SMR process. For hydrogen production may be possible one of the criteria to consider in the production of hydrogen is emissions of greenhouse gases (specially CO<sub>2</sub>), the SMR process emits 68.2 kg CO<sub>2</sub>/GJ and will issue that amount produced 588.24 MW of hydrogen per km<sup>2</sup> at a cost of US \$982/Ton H<sub>2</sub>. In a process which includes the capture of CO<sub>2</sub> by the same technology SMR only 22.8 kg CO<sub>2</sub>/GJ be issued, however, the cost of production increases to US \$1,575/Ton H<sub>2</sub> [5]. It should be noted that the construction of plants natural gas reforming at low scale such as 0.27 millions Nm<sup>3</sup>/day where hydrogen cost is around US \$6.0-7.5/GJ [7].

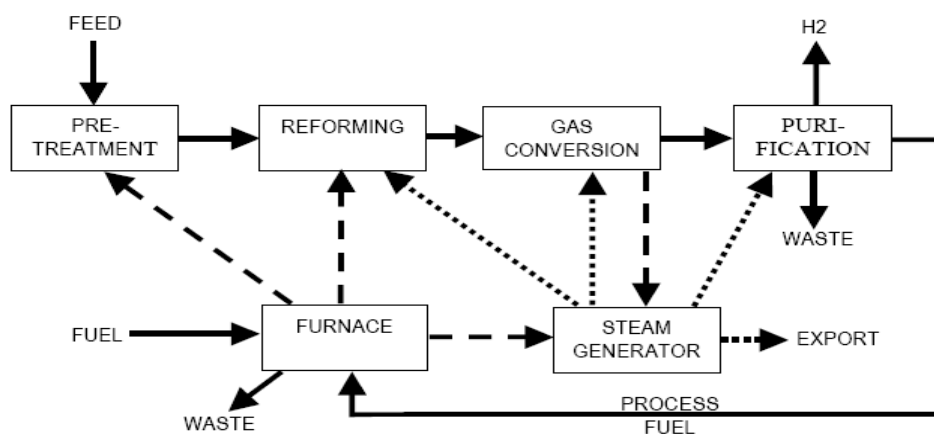
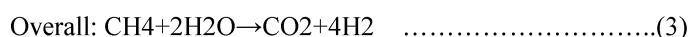


Figure 1. Schematic of SMR Process Showing Heat and Materials Integration

Mexico is one of the largest consumers and producers of natural gas, some of this gas used to produce hydrogen is fed into the hydrodesulfurization plants at refineries in the country, and according to the specific requirements of each refinery infrastructure is developed the safe and efficient hydrodesulfuration unit to provide larger volumes of hydrogen to plants diesel HDS [8]. SMR in plants, CO<sub>2</sub> captured can be categorized before, during and after combustion; eliminating CO<sub>2</sub> before it, when combustion is performed using oxygen instead of air, generating a concentrated stream of CO<sub>2</sub> is compressed for transport and subsequent kidnapping [6].



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During the compression process of 1 kg hydrogen caused by the SMR process is consumed between 5.0-5.5 m<sup>3</sup> of natural; 4.0-4.5 kg of water, 0.7 to 0.9 kWh of energy and emissions are 9.5 kg of CO<sub>2</sub>/kg of hydrogen. In the case of liquefied hydrogen energy consumption in the liquefactions becomes 11-13 kWh per kilogram of hydrogen, this high consumption is reflected in an increased amount of CO<sub>2</sub> emissions of 35-38 kg of CO<sub>2</sub>/kg of hydrogen. Although the ideal goal is to reduce total emissions of greenhouse gases for the production of hydrogen, this will be possible only until the renewable energy technologies like PV or wind are developed more efficiently. Currently the process of reforming of natural gas is the best opinion for hydrogen production in Mexico by having the infrastructure and sufficiently effective [9].

## 2.2. Hydrogen gasification of coal

This technology is competitive in places where oil and natural gas are expensive. It is used to produce synthesis gas from waste oil and coal, although they can feed the refinery waste, biomass and municipal solid waste.

The cost of raw material feed for the gasification process accounts for 25% of the final cost of hydrogen, despite the abundance of coal reserves in the world, it has a significant environmental impact as 132.6 kg CO<sub>2</sub>/GJ generating 588 MW per km<sup>2</sup> at a cost of US \$1,621/Ton of hydrogen. If this method is performed with CO<sub>2</sub> capture would emit into the atmosphere only 37.5 kg CO<sub>2</sub>/GJ generating 588 MW of hydrogen per km<sup>2</sup> but the cost would rise too much as US \$3,114/Ton of hydrogen [5].

Compression of 1 kilogram of hydrogen obtained from this process consumes fuel 6.0-7.0 kg coal/ kg H<sub>2</sub>, 9 kg of waste and 0.7 to 0.8 kWh of energy issuing 22 kg CO<sub>2</sub> and 13-14 kWh for emitting liquefaction 46 kg CO<sub>2</sub> [9].

## 2.3. Hydrogen electrolysis

Decomposition of water into hydrogen and oxygen. The electrolyte is a solution of KOH in water; hydrogen is produced at the cathode with nearly 100% purity at low pressures. Considering power consumption efficiency 100% is 40 kWh/kg hydrogen, but in practice is higher energy consumption. The main disadvantage of electrolysis is the cost of electricity. For renewable energy that dominates is the cost of investments in photovoltaic systems or wind to generate electricity that is used in the electrolysis process, in the case of photovoltaic system can be 85% the price of hydrogen [7].

The total capital investments for the installation of hydrogen production by electrolysis with electricity supply network related to its size, for a plant with a capacity of 2.8 million Nm<sup>3</sup>/day, the total investments cost TCI is US \$2.95/GJ and large plants at 6.75 million Nm<sup>3</sup>/day the TCI is US \$30.97/GJ. Resource consumption per 1 kg of hydrogen of 55-60 kWh electricity and generates emissions of 41 kg of CO<sub>2</sub> [7].



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### 3. Results and Discussion

Table 1 shows a summary of the estimated costs of hydrogen production in each technology listed above, showing the cost of production and cost to the consumer the estimate is made for a centralized and each of the technologies has transportation distance of 100 km from the hydrogen production plant to the point of delivery [9]. Each of these three scenarios it is observed that the difference in cost between hydrogen production and hydrogen compressed liquid is more than double its generating greenhouse gases, consequently greater, itself one of the objectives is to reduce greenhouse gases, we noted that production of liquid hydrogen is not a good economic or environmental option.

Table 1. Estimated cost of centralized hydrogen production and delivery to user as a liquefied compressed gas [9].

Production technology	Cost of production, \$/kg H <sub>2</sub>			Cost to consumer, \$/kg H <sub>2</sub>			CO <sub>2</sub> emission, kg CO <sub>2</sub> /kg H <sub>2</sub>
	I	II	III	I	II	III	
<b>Compressed H<sub>2</sub></b>							
SMR (natural gas)	1.2	1.9	2.6	1.6	2.4	3.1	9.5
Coal Gasification	1.8	2.0	2.2	2.3	2.5	2.7	21.8
Electrolysis (energy grid)	4.3	6.7	9.2	4.8	7.2	9.7	41.1
<b>Liquefied H<sub>2</sub></b>							
SMR (natural gas)	2.9	3.7	4.4	3.1	3.8	4.5	17.4
Coal Gasification	3.8	3.9	4.1	3.9	4.1	4.2	30.0
Electrolysis (energy grid)	5.7	8.6	11.6	5.9	8.8	11.7	48.6

I. Optimistic estimate, II. Moderate y III. Pessimistic.

The process of electrolysis using energy from the power supply that has a high cost in either scenario and the emissions of greenhouse gases into the atmosphere is much higher even in liquid hydrogen as compressed gas because the electricity used and this process is generated from fossil fuels. Then, gasification is a technology known but cheap and emissions of greenhouse gases are high for the case of compressed hydrogen gas for liquefied hydrogen.



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The variation in costs to consumers are more accessible when the production of hydrogen through the process of performing of natural gas, since the variation between production costs and consumers costs is US \$0.4, and has lower emissions of greenhouse gases than the process of gasification and electrolysis.

According to table 1, the SMR process is the best option for hydrogen production because de production costs in any of the three scenarios are lower and emissions of greenhouse gases ( $\text{CO}_2$ ) are minimal and technology is completely known. The development of this technology in every region of the planet is determined by policies to reduce emissions of greenhouse gases and objectives of the Kyoto Protocol compliance. The availability of the raw material of SMR process is a fact that will determine the feasibility of the process, natural gas is considered the least polluting fossil fuel opposed to oil and coal so that their abundance is a important factor, for example United Arab Emirates produce about 3 billion cubic feet per day of natural gas and Mexico 5,394.6 cubic feet per day, which only 98% is used and the rest is sent into the atmosphere [14-15]. Despite of the increased production of natural gas in the UAE, according to the International Energy Agency, Mexico has three times the hydrogen production capacity of refineries in the UAE [16]. The hydrogen production plants operate at factor of 90% can produce 36,000 GJ of  $\text{H}_2$  per day, enough to power 500,000 PEMFCV or small scale able to produce 108 GJ of  $\text{H}_2$  per day, enough to feed 2,200 PEMFCV. However, the large scale hydrogen production is better to transportation demand and power generation [17]. The SMR process efficiency is between 65-75% which is measured in terms of fuel and electricity that they feed. Since the process is highly exothermic SMR produces more steam than it consumes, if the steam generated by the process used in other plant services, this would be at least 10% more efficient, competing with electrolysis renewable sources. The cost of production by SMR varies according to the price of natural gas if consumed at the site where it is produced would cost US \$0.65/kg  $\text{H}_2$  [17].

According to governments regulations in each country to shift to cleaner energy production based on the use of natural gas as fuel of hydrogen production, there are three scenarios in percentage (%) of the use of natural gas to produce hydrogen through the process SMR. These scenarios range from 10%, 50% and 100% use of NG to produce hydrogen. Figure 1, shows the cost that would generate hydrogen using different percentages of NG, the analysis was made for an annual production of  $1.1 \times 10^9$  GJ/ year in the UAE, at present the annual production in Mexico is  $2.1 \times 10^9$  GJ/year. Watching the scene using 100% natural gas for hydrogen production, the capital cost is about 50% lower than he scenario using 10% natural gas, operating cost and maintenance (O&M) and the cost of compression and storage are lower, US \$0.45/GJ and US \$0.265/GJ respectively, only the cost of natural gas is the same. Therefore the total cost of hydrogen production at 100% using of natural gas is US \$6.15/GJ, which, compared with





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the literature is in the range of US \$6.0-7.5/GJ for large scale plants that produce from 1.34 to 25.4 million Nm<sup>3</sup>/day of hydrogen [17].

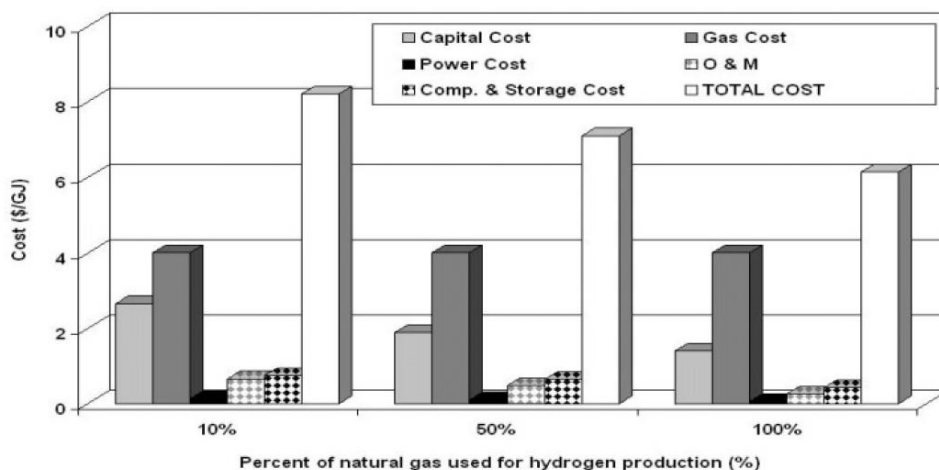


Figure 2. Breakdown of production costs of hydrogen with various percentages of current natural gas production.

Although the price of electricity for hydrogen production by electrolysis is high and emissions of greenhouse gases are higher among these three technologies, there are plants where the production of hydrogen is not the final product basics. An example is the production of hydrochloric acid, which is carried out by electrolysis where common salt or sodium chloride NaCl mixed with demineralised water to form an aqueous mixture with salt (salt magma) and form sodium chloride brine. To this solution should remove impurities and filtered to pass the area of electrolytic cells. Plants producing hydrogen by electrolysis operating with a solution of potassium hydroxide and hydrochloric acid productions works with a solution of sodium chloride (NaCl), both are brine which uses as electrolyte. Of sodium chloride brine passing through the electrolysis process are obtained the following chemicals: chlorine wet cell liquor and hydrogen damp and water that contain dissolved sodium hydroxide. The main product, chlorine, is cooled, filtered, washed and dried. Chlorinated water which resulted in the washings is used in the production of sodium hypochlorite and chlorite passed once dry blending the area [10]. The technology currently used in the cells is known as “DeNora” corresponding to the Italian company owns the patent, but other technologies such as Stuart IMET Electrolyser (Canada), Norks Hydro (Norway) and Uralkhim mash (Russia) all with efficiencies above 500 m<sup>3</sup>/hr of hydrogen and 0.1 to 5 MPa [11].

### 3.1. Case Study



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The hydrogen produced by electrolysis is still an expensive process for the cost of grid electricity for the plant is estimated in 2650 kW/Ton  $\text{Cl}_2$ , placing it as the second largest consumer of electricity in the state of Jalisco, however, the greater benefit is the sale of hydrochloric acid 30%, liquid chlorine, sodium hypochlorite and soda caustic. The composition of the hydrogen obtained is 99.999% pure, suitable for use in devices such as fuel cells and auto supply power. Among the benefits of the current hydrogen is supply to boilers for generating steam to heat and supply to plant where hydrogen is 30% of the mixture and 70% natural gas mixture as feedstock supply companies for through tubing to 0.4 psi pressure for the process of hydrogenation of fats and oils. The hydrogenation process consumes about 2 million cubic meters of hydrogen per year, between 150,000 and 250,000  $\text{m}^3$  each month, according to demand, the cost of hydrogen in a year is about \$ 4 billones (US \$ 300,000), US \$350-500 thousand per month [12]. The price of 1 me of hydrogen produced by electrolysis using the basic process of generation in this business is \$ 1.80 significantly lower for the consumer compared to the one shown in table 1 in any of the three scenarios, since the cost are borne y sales of hydrochloric acid, chlorine, sodium hypochlorite and caustic soda [10].

According to data from 2008 to 2011, each month will produce about 84 ton of hydrogen, approximately 83% of the hydrogen is used to generate heat, hydrogenation of fats and oils and the production of hydrochloric acid from the same plant. The remainder of production has no use a raw material or as energy, but must be vented to atmosphere for process safety. The potential of the remaining 17% hydrogen to generate energy could be used in fuel cells to supply power to the plant. A common fuel cell of 5kW in Mexico cost US \$15,000 (\$200,000 pesos) and needs a supply of maximum flow output of 64 lt/min. Evaluating the hydrogen production conditions of the plant this would generate 57 times per day flow required by the fuel cell.

“The ability to offset peak electricity usage with an emission-free fuel cell system will create significant savings, while reducing our environmental footprint”. Mark Yamauchi, TMS Facilities Operations Manager.

The background to the application of this technology is shown by the company Ballard Power Systems, which developed a system of hydrogen, a by-product of the production process of hydrochloric acid  $\text{HCl}$ , could be supplied in fuel cells feed with hydrogen and power generation electrical, which has been shown is a prohibitively expensive fuel for these companies that produce  $\text{Cl}_2$  through electrolysis. According to the proposal CLEARgen<sup>TM</sup> Ballard, electricity accounts for 70% the cost of production of chlorine [13].

According to Mexichem S. A. de C. V. company, the cost of electricity is very high, making this company the second largest energy consumer in the state. If the hydrogen vented to the atmosphere could be recovered and used to generate electricity, then the hydrogen would get more value than it now has a raw material or fuel.





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#### **4. Conclusions**

Therefore, the total cost of hydrogen production at 100% using of natural gas is US \$6.15/GJ, which, compared with the literature is in the range of US \$6.0-7.5/GJ for large scale plants that produce from 1.34 to 25.4 million Nm<sup>3</sup>/day of hydrogen [17]. The operating conditions of gas natural in Mexico for the production of hydrogen compared to the United Arab Emirates, 1.1X10<sup>9</sup> GJ/year, and show that it is feasible to use the oil for hydrogen production in Mexico with 2.1X10<sup>9</sup> GJ/year. The most likely is a transition with the highest percentage of use of gas natural for hydrogen production via SMR process is the cheapest compared to other processes, besides being friendlier to the environment. The SMR process can also be more efficient if the current of steam generated is used in other plan services, giving use the product as in the case of the company Mexichem, where the potential for generation of electricity through the use of hydrogen they get as by-product in the process serve as feed for fuel cells; mitigate electric power consumption of the network, allocating the percentage that supply boilers to fuel cells that would deliver clear energy.

#### **5. Acknowledgments**

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